VISIT…

LUBRICATED WEAR

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INTRODUCTION

The prime function of a lubricant is to reduce friction, wear, and general surface damage by prevention of solid-solid contact of asperities on opposing surfaces. When the surfaces are metals, the lubricant must inhibit the formation of any strong metallic junctions that would lead to adhesive wear. By definition, any gas (vapor), liquid, or solid can serve as a lubricant as long as it reaches the surface and physically keeps the asperities separated.

Liquid lubricants scavenge wear debris and remove heat from contacting surfaces. The latter reduces operating temperature, resulting in the formation of thicker oil films and/or a lower demand on the lubricant additives. Scavenging of wear debris lessens the chance of interaction of small wear particles to form larger, work-hardened particles which can cause abrasive wear, higher surface temperatures, and mechanical destruction of the surface antiwear film.

ADHESIVE WEAR

Adhesive wear occurs under lubricated conditions when the hydrodynamic or elastohydrodynamic (EHL) film is so thin that surface asperities penetrate the film. Despite the presence of intervening lubricant between two asperities on a collision path, high hydrodynamic pressures elastically deform the metal and squeeze out the lubricant until only a very thin surface (boundary) film separates the surfaces.[1] Concurrently, asperity contact area grows due to high normal and tangential stresses on the metal (plastic as well as elastic deformation can occur) so that the trapped boundary film may be stretched until it ruptures, thereby allowing the formation of a metal-metal junction. In addition, high-shear stresses cause considerable local heating, which weakens the adsorption forces of the surface film. Mineral oil molecules and simple polar compounds desorb under these high temperatures, again allowing metal-metal contact.

A number of mathematical models for lubricated wear are based on modifications of the equation for unlubricated adhesive wear. The usual mathematical model for adhesive wear rate (V/d) may be modified to:[2]

$$\frac{V}{d} = K_m A_m = K_m \alpha A = K_m \alpha \frac{W}{H} \qquad (1)$$

where V is the volume of wear, d is the sliding distance, K_m is the dimensionless adhesive wear coefficient for the particular sliding couple free of any surface contamination, A_m is the true area of metallic contact within the total true area of contact A, W is the load, H is the hardness, and α is the fractional defect of the surface film. Lubricant effectiveness in mitigating wear is expressed entirely by α, although the metal is indirectly involved through lubricant-metal interactions. Even under nominally dry sliding conditions, adsorbed gas molecules or oxide film function to some extent as a lubricant so that αK_m is reduced to a typical value of 1×10^{-3}. K_m for most metals is of the order of 0.1 to 0.2.[3]

A model for a defect in the surface film assumes that the energy of adsorption-desorption is critical to the effectiveness of the lubricant molecule on the surface.[2] Parameter α may be expressed as

$$\alpha = \frac{X}{Ut_o} e^{-E/RT_s} \qquad (2)$$

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where X is the diameter of the area associated with an adsorbed lubricant molecule, t_o, is the fundamental time of oscillation of the molecule in the adsorbed state, U is the sliding velocity, E is the energy of adsorption, T_s is the surface temperature, and R is the gas constant. Combining with Equation 1.

$$\frac{V}{d} = K_m \frac{X}{t_o H} \cdot \frac{W}{U} \cdot e^{-E/RT_s} \tag{3}$$

A modification of the equation for lubrication by gases correlates the wear results of graphite in the presence of hydrocarbon vapors at varying vapor pressure, and the vapor pressure for a given wear rate correlates with the heats of adsorption of hydrocarbon, alcohol, carbon tetrachloride and water vapors.[4]

The following expression was derived for the presence of an antiwear additive in a base oil:[5]

$$\left(\frac{V}{d}\right)_c = \frac{e^{-\frac{\Delta E}{RT_s}}}{e^{\frac{\Delta S^\circ}{R}}} \left[\frac{\left(\frac{V}{d}\right)_b - \left(\frac{V}{d}\right)_c}{C}\right] + \left(\frac{V}{d}\right)_b \frac{e^{-\frac{\Delta E}{RT_s}}}{t_o'} \tag{4}$$

where $(V/d)_c$ and $(V/d)_b$ are the wear rates for additive concentration C and for base oil, respectively, ΔS^o is the entropy change for the system, and the t_o' is the ratio of the fundamental oscillation times of additive and solvent on the surface. Figure 1 plots the wear rate of a copper pin-on-steel against the quantity in brackets of Equation 4 for stearic acid solutions at 77°C. From the slope and intercept, the adsorption-desorption equilibrium constant K can be calculated from the expression

$$K = e^{\Delta S^\circ/R}\, e^{\Delta E/RT_s} \tag{5}$$

Figure 2 is a plot of the calculated values of the equilibrium constant and $\Delta E(\Delta E = E_a - E_b)$ from wear tests of *n*-octadecanol, *n*-octadecanoic acid, and *n*-octadecylamine solutions in *n*-hexadecane using AISI-1020 steel surfaces in a pin-on-disk machine. The values are plotted against independently published surface potential measurements of the same additives on steel surfaces.[6] The order amine > acid > alcohol agrees with friction measurements of monolayers and wetting measurements of adsorbed films from *n*-hexadecane on metal[7] and with four-ball wear results.[8]

Collectively, these results support the concept that adsorbed surface films of long-chain polar compounds reduce adhesive wear and that the magnitude of the energy of adsorption is a controlling factor. For antiwear additives that function by chemical reaction with the metal substrate, reaction rates are probably fast compared to desorption of the reaction product, so that desorption energy of the reaction product is controlling and the model remains applicable.

CORROSIVE CHEMICAL WEAR

Antiwear and extreme pressure additives generally function by chemical reaction with surfaces. For example, organic disulfides form an iron mercaptide on steel surfaces under mild conditions[9] and iron sulfide under more severe operating conditions.[10] Likewise, organophosphates, such as tricresyl phosphate, react with iron surfaces to produce iron organophosphate under mild operating conditions and iron phosphate under severe conditions of high-load and high-surface temperature.[11]

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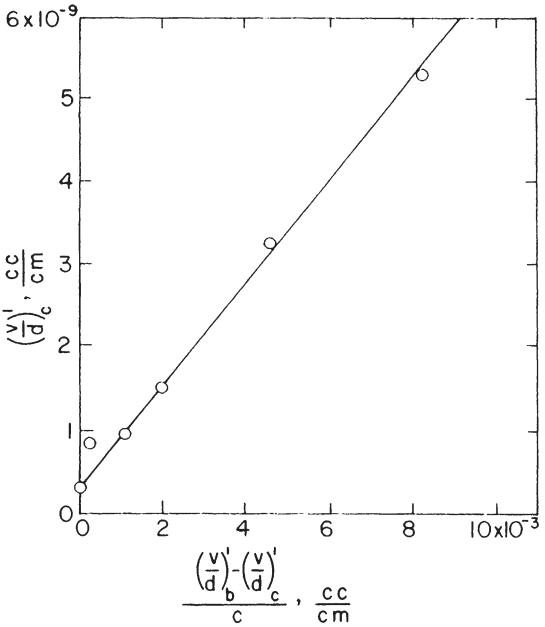

FIGURE 1. Wear rate of copper pin as a function of stearic acid concentration at 77°C. (From Rowe, C. N., *ASLE Trans.,* 13, 179, 1970. With permission.)

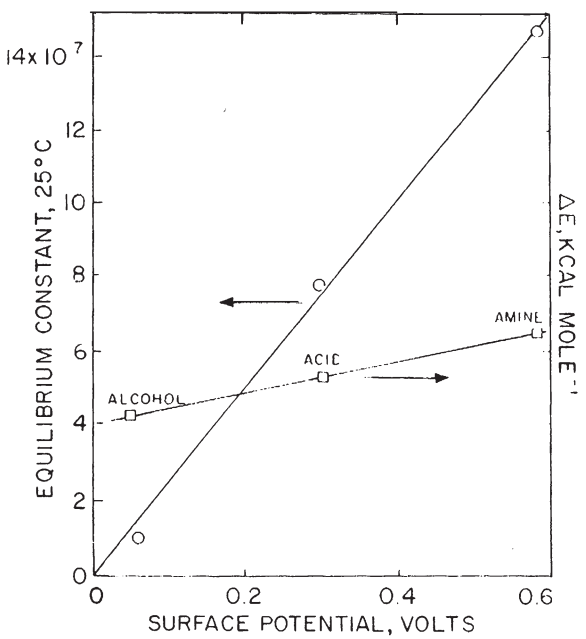

FIGURE 2. Correlation of calculated adsorption parameters from wear tests with surface potential measurements on steel surfaces. (From Rowe, C. N., *ASLE Trans.,* 13, 179, 1970. With permission.)

During relative motion of surfaces, some reaction product is lost by shearing or mechanical action, giving rise to chemical wear. Generally, the term corrosive wear is used when chemical wear is the dominant wear mode and it exceeds by a wide margin (>10 to 1) the

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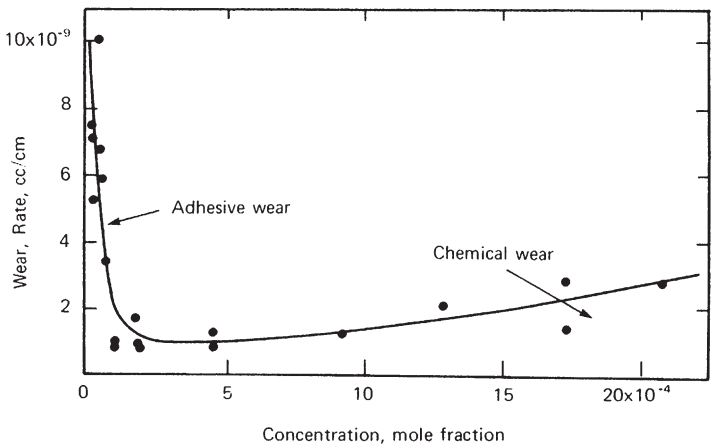

FIGURE 3. Effect of concentration on wear rate of a copper pin with zinc *0,0*-diisopropylphosphorodithioate additive in cetane. (From Rowe, C. N., *ASLE Trans.,* 13, 179, 1970. With permission.)

amount required to control adhesive wear. Under normal circumstances, however, the amount of corrosive wear is only a small fraction of the adhesive wear that would occur if the antiwear or EP additive were not present.

Corrosive wear may occur by selective chemical reaction with one component in a bearing alloy followed by the reaction product dissolving in the oil. An example is the selective loss of lead in copper-lead connecting rod bearings by halide scavengers from the leaded fuel.[12] Where corrosion is a problem, additives are added to the oil to prevent the chemical reactions, either by inhibiting oil oxidation or by surface adsorption of metal deactivators.

ADHESIVE WEAR-CHEMICAL WEAR BALANCE

A balance may be obtained between adhesive and chemical wear under optimum conditions. Under operating conditions in which chemical reactivity of the lubricant is very low the adhesive wear process will dominate; alternatively, corrosive wear will dominate when chemical reactivity is excessive. An optimum balance is found as additive concentration is varied. Figure 3 shows the wear rate of a copper pin as a function of zinc *0,0*-diisopropylphosphorodithioate concentration in *n*-hexadecane.[5] At extremely low-additive concentrations, the surface is only partially protected and adhesive wear predominates. At high-additive concentrations, an excessively thick chemical reaction film is formed and worn during sliding.

More severe sliding conditions require greater chemical reactivity or higher additive concentrations for achieving the optimum balance between adhesive and chemical wear. Consequently, the curve in Figure 3 will shift to the right, as shown in Figure 4. The observed wear with reactivity A will be controlled by chemical wear for severity I, optimum balance of adhesive and chemical wear in II, and adhesive wear in III. This figure illustrates the difficulty frequently encountered in rating antiwear additives among various bench wear tests and field applications arising from the variation in severity at the rubbing interfaces.

Definition and measurement of chemical reactivity at a metal surface is difficult because reaction rate is exceedingly low under normal ambient conditions. Figure 5 plots wear vs. corrosion rate of an electrically heated iron wire for a variety of organic phosphites and phosphates in a refined bright stock oil.[13] Others measured the rate of decomposition of zinc *0,0*-dialkylphosphorodithioates and found correlation between the wear rate of a copper pin sliding against steel vs. the rate of hydrogen sulfide formation.[14]

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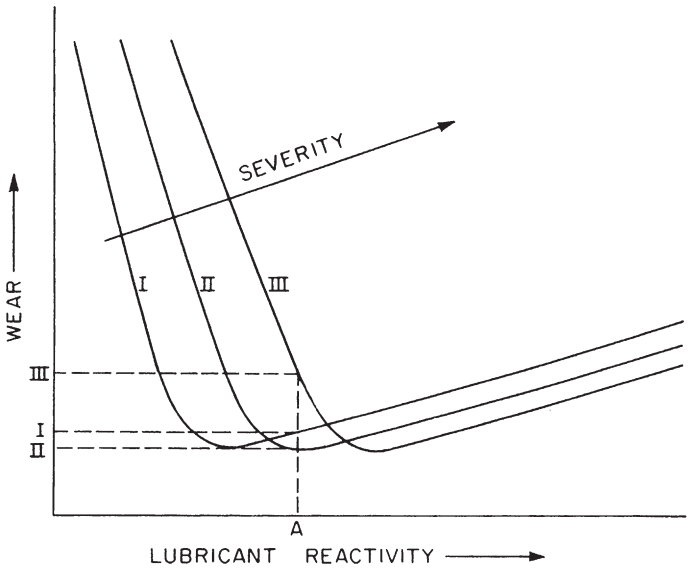

FIGURE 4. Schematic plot illustrating effect of severity of sliding on adhesive-chemical wear balance.

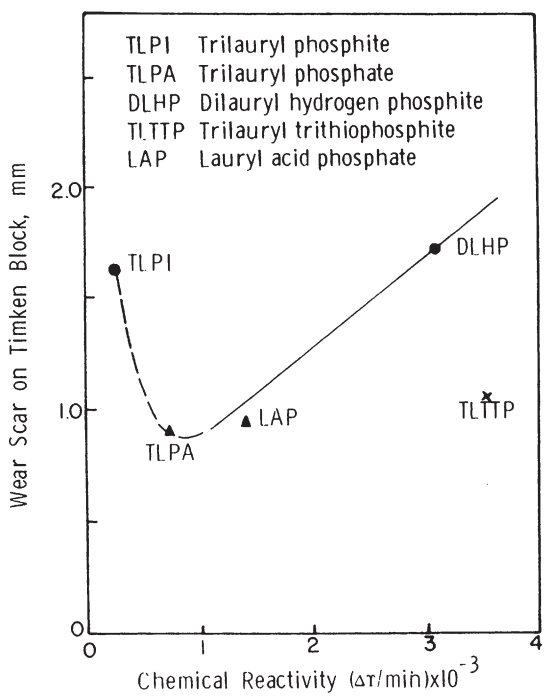

FIGURE 5. Relation between wear and chemical reactivity for phosphorus compounds. Chemical reactivity defined as rate of change of radius (Δr/min) in hot wire method. (From Sakurai, T. and Sato, K., *ASLE Trans.,* 13, 252, 1970. With permission.)

Figure 6 correlates load-carrying capacity, expressed as ratio of Mean Hertz Load with and without EP additive, with chemical reactivity as measured by the hot wire method for two types of EP additives.[13] Chemical reactivity is expressed as the ratio of rate constants

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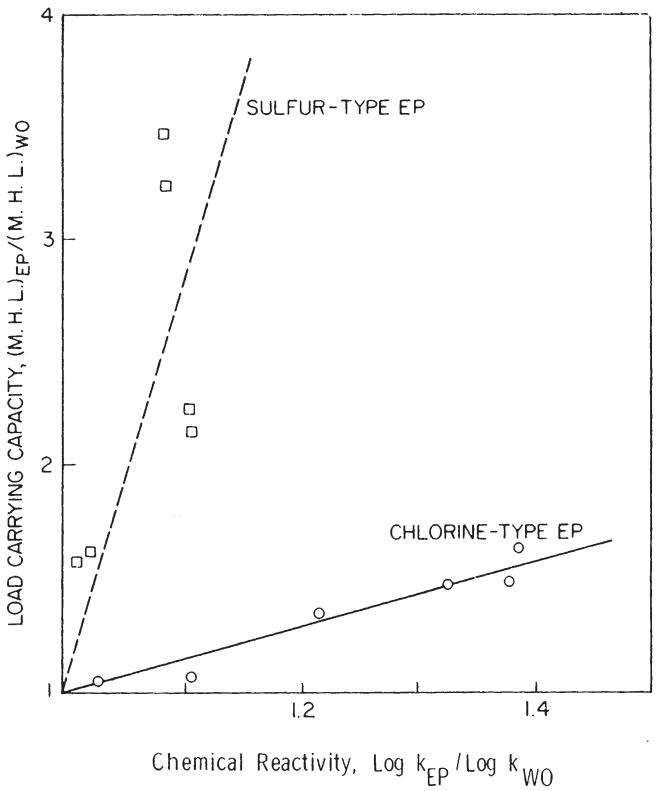

FIGURE 6. Dependence of load-carrying capacity on chemical reactivity. (From Sakurai, T. and Sato, K., *ASLE Trans.,* 13, 252, 1970. With permission.)

k with and without EP additive, and k is the rate of change of radius of the electrically heated wire. The separate curves for the sulfur- and chlorine-containing compounds suggest that the effectiveness of the surface reaction product is also an important parameter.

Unfortunately, comprehensive guidelines for achieving maximum wear life are often not available due to a lack of understanding of many parameters including the following:

1. Local surface temperatures and pressures
2. Catalytic properties of deformed metal and newly created surface
3. Chemical reactions between the additive and the metal
4. Possible role of oxygen in the chemical reactions
5. Surface reaction and diffusion kinetics
6. Lubricant residence time in the contact zone
7. Optimum surface film thickness for maximum antiwear response
8. Properties of the surface film that control its rheology, shear strength, and adherence to the metal

With a completely formulated lubricant, additive interactions can occur in the bulk phase as well as in competing reactions with the surface, making the composition of the boundary film and its properties even more complex. In addition, a given lubricant is frequently required to lubricate different types of contacts with varying levels of severity and different metallurgies that can give entirely different surface reaction products. Nevertheless, various load-carrying and wear test results have led to valuable guidelines for producing effective additives to satisfy increasingly severe performance demands.

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Table 1
HEAT OF ADSORPTION OF ADDITIVES ON IRON OXIDE

Additive	cal × 10^{-3}/g Fe_2O_3
$[CH_3(CH_2)_{11}-S-]_2$	4.9
$[-(CH_2)_4COOC_2H_5]_2$	7.0
$[-S-(CH_2)_2COOC_2H_5]_2$	11.4

From Forbes, E. S., Allum, K. G., Neustadter, E. L., and Reid, A. J. D., *Wear,* 15, 341, 1970. With permission.

Kinetics of Surface Reactions

Kinetics of chemical reactions of antiwear and EP additives with sliding surfaces are important for maximum effectiveness. Reaction of radioactive S^{35} EP additives with rubbing surfaces in a pin-on-disk machine has been investigated, modeled mathematically, and various rate constants calculated. References 15 to 18 constitute a formidable beginning to sort out the kinetics of adsorption, chemical reactions, and wear of reaction products in contact areas.

The adsorption and the configuration of the adsorbed molecule before chemical reaction takes place are important.[19] Diester sulfides having the structure

$$[—S—(CH_2)_nCOOC_2H_5]_2$$

where n = 1, 2, or 3 were found to be effective antiwear compounds at low concentrations. At high concentrations, however, they possess poor EP properties, so that wear is adhesive. Electron probe microanalysis showed appreciable sulfur present on the wear scar at low concentrations but very little at high. Heats of adsorption in Table 1 show that the ester groups contribute more to adsorption than do the sulfur atoms. Evidently, at low concentrations both sulfur and ester groups lie on the surface and the sulfur is available for forming iron sulfide. At high concentrations, the more strongly adsorbed ester group displaces the sulfur atoms, thereby eliminating sulfur from chemical reaction with the surface.

The importance of the kinetics of additive-metal chemical reactions may be illustrated in comparison of phosphorus and sulfur EP additives in CRC L-37 and L-42 hypoid gear tests. Sulfur compounds generally function best at high-speed/low-load test (L-42) conditions while phosphorus compounds function best at low-speed/high-load test (L-37) conditions. High-speed operation results in short time intervals between repeated contacts so that the reaction kinetics of sulfur compounds may be more favorable for the L-42 test.

Temperature

Temperature is the key parameter in many lubrication mechanisms for controlling wear. Temperature determines the viscosity of the lubricant and its ability to generate a viscous film for keeping the surfaces separated. As temperature increases, the chance of asperity interactions increases and greater demand is placed on the surface film.

Surface temperature determines the reaction kinetics of antiwear and EP additives with rubbing surfaces. Many EP additives require some minimum threshold temperature to become effective. Providing the reaction is endothermic, a further increase in surface temperature can lead to excessive chemical reaction and possible chemical wear (Figure 4).

At excessively high surface temperatures, however, the following factors can lead to a loss in additive response: (1) a decrease in adhesion to the metal substrate, (2) increased

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desorption due to greater oil solubility, and (3) a modification of the rheology or shear properties of the film. As the surface film becomes less effective, the increased metallic contact leads to higher friction, even higher surface temperatures, and the onset of catastrophic wear. This has become known as the transition temperature phenomenon.[20]

Load

Wear rate is proportional to load in Equation 1 because the true area of contact is proportional to load under thin film conditions. As the number of asperity contacts increases with increasing load, a point is eventually reached where the diminishing lubricant film can no longer support the load. This is the point of transition from mild (acceptable) wear to ineffective lubrication and catastrophic adhesive wear.

Wear transitions with increasing load are common in the four-ball wear test. The value of the dimensionless wear coefficient K,

$$K = \alpha k_m = \frac{VH}{dW} \tag{6}$$

for a paraffinic oil at 15-kg load and 1 hr was 7.8×10^{-8}, while at 60- and 70-kg load and 1 min tests the K values are 6.6×10^{-4} and 6.9×10^{-4}, respectively.[21] Wear rate above the transition is about 10,000 times higher.

A plausible mechanism for the abrupt transition in wear may be found in the behavior of wear debris. Below the load transition, generated wear particles are able to escape the geometrical area of contact without extensive interaction with each other. As the number of metallic contacts and resultant wear particles increase, the rate of generating wear particles eventually exceeds the rate at which they can escape without interaction and aggregation. Wear particle interaction then causes a rapid deterioration of the lubricant surface film, probably by both a mechanical action and a temperature rise at the surfaces.

Sliding Velocity

Sliding velocity can have opposing effects. At low sliding velocity an increase in velocity decreases wear because of the generation of micro-EHL films[1] and the reduced chance of squeezing the surface film from between colliding asperities.[22] Equation 3 suggests that wear is inversely proportional to sliding velocity. At high sliding velocities, high surface temperatures may be experienced since temperature rise is proportional to sliding velocity. Comments made previously on temperature apply.

Wear Coefficients

The value of K ($K = \alpha K_m$) for unlubricated AISI-52100 steel is of the order of 1×10^{-3}.[23] For antiwear and EP additives, K values are of the order of 10^{-9} to 10^{-7} in four-ball wear tests.[24] Table 2 gives K values for zinc dialkylphosphorodithioates and typical phosphorus and sulfur compounds in the four-ball wear test and shows that the K ranking is roughly

$$\text{Zinc dialkylphosphorodithioates} < \begin{matrix}\text{phosphorus}\\ \text{compounds}\end{matrix} < \begin{matrix}\text{sulfur}\\ \text{compounds}\end{matrix}$$

These results.show that effective lubricants can reduce wear to about one millionth of that under unlubricated sliding conditions

ABRASIVE WEAR

Abrasive wear results from a cutting action by (1) a rough, hard surface sliding against

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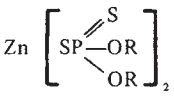
Table 2
WEAR COEFFICIENT K

Additive	Wear scar diameter (mm)	Wear coefficient K ($\times 10^{-8}$)
Zinc Dialkylphosphorodithioates		
		
R = Isopropyl	0.258	0.17
R = 2-Ethylhexyl	0.296	0.43
R = *n*-Dodecyl	0.290	0.37
Phosphonates		
$(R_1O)_2P(O)R_2$		
R_1; R_2		
Butyl; H	0.64	14.1
2-Ethylhexyl; H	0.36	1.2
Butyl; phenyl	0.48	4.2
Phosphates		
Tributyl	0.47	3.9
Tricresyl	0.28	0.29
Disulfides		
Dibenzyl	0.560	8.1
Di-*n*-butyl	0.855	46.0
Di-*n*-dodecyl	0.623	12.6

Note: Four-ball test, 15 kg, 1500 r/min, 50°C, 60 min.

From Rowe, C. N., *Wear Control Handbook,* Peterson, M. B. and Winer, W. O., Eds., American Society of Mechanical Engineers, New York, 1980, chap. 6. With permission.

a softer surface, or (2) contaminant hard particles trapped between sliding surfaces. Hydrodynamic, or elastohydrodynamic, lubricant films either sufficiently thick to separate the surfaces in (1) or thicker than the largest hard particles in (2) will greatly reduce abrasive wear.[25] Abrasive wear in lubricated systems is controlled either by providing a lubricant of the appropriate viscosity for generating a sufficiently thick lubricant film, or by using adequate filters for removal of unavoidable hard particle contamination.

If adhesive wear particles remain in the contact area, chances are good for the formation of larger particle aggregates which can undergo work-hardening and cause abrasive wear. Liquid lubricants can flush the adhesive wear particles out of the contact area and prevent the series of steps that lead to abrasive wear. With operating conditions and systems where it is impossible to have thick lubricant films, antiwear and EP additives may offer some protection through the generated surface film, both by its thickness and its reduction of adhesive wear.

CONTACT FATIGUE

Fatigue is associated with cyclic loading as encountered with rolling element bearings, gears, and valve trains. Cyclic deformation of the contacting surface leads to the initiation

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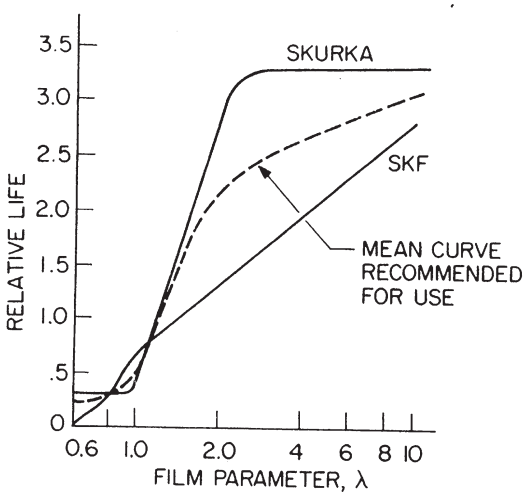

FIGURE 7. Relative fatigue life as a function of film parameter, λ. (From Bamberger, E. N., Harris, T. A., Kacmarsky, W. M., Moyer, C. A., Parker, R. J., Sherlock, J. J., and Zaretsky, E. V., *Life Adjustment Factors for Ball and Roller Bearings — An Engineering Guide,* American Society of Mechanical Engineers, New York, 1971. With permission.)

and propagation of microcracks. Subsurface crack initiation is generally in regions of maximum shear stress and is often associated with inclusions in the metal. Surface imperfections, imbedded debris, scratch marks, dents, and contaminant hard particles in the lubricant can act as stress initiators for surface microcracks. Development of a network of cracks via crack propagation results in spalling or pitting, which are forms of fatigue wear.

Physical and chemical properties of the lubricant play a significant role in fatigue wear.[26] Specific film thickness, λ, which is the ratio of EHL film thickness to the composite surface roughness, is considered to be an important parameter affecting the fatigue life of bearings.[27–29] Since λ is a function of lubricant viscosity and viscosity-pressure coefficient, fatigue can often be controlled by selecting lubricants of proper viscosity. Figure 7 plots relative fatigue life as a function of the film parameter, or specific film thickness.[30]

Effect of Water

Small amounts of water added to lubricants may significantly reduce the fatigue life of ball and roller bearings as summarized in Table 3. With varying water content in an SAE-20 rust and oxidation-inhibited mineral oil in tapered roller bearing tests at 2.03 GPa (290,000 psi) Hertz stress, relative life (L_{Rel}) follows the expression:

$$L_{Rel} = \left(\frac{100}{C}\right)^{0.6} \tag{7}$$

where C is water concentration in parts per million (ppm) and the relative life is one at 100 ppm.[31] The effect of added seawater to commercial hydraulic fluids on the fatigue life of angular contact ball bearings at 2.27 GPa (330,000 psi) Hertzian stress is found in Reference 32. Figure 8 is the present writer's plot of the log of life/EHL film thickness ratio against the log of water content in the oils as received. A least square analysis of the data shows that

$$\frac{L_{10}}{h} = \text{constant } C^{-0.42}$$

$$\frac{L_{50}}{h} = \text{constant } C^{-0.68} \tag{8}$$

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Table 3
EFFECT OF WATER IN LUBRICANTS ON ROLLING CONTACT FATIGUE LIFE

Lubricant description[a]	Water content of oil(%)	Fatigue life reduction (%)	Test equipment and Hertzian stress	Ref.
SAE 20 rust and oxidation inhibited mineral oil (0.01%)	0.04	48	Tapered roller bearing 2.03 GPa (0.29 ×□0^6 psi)	31
Mineral oil-based	0.1	45	Angular contact bearing	
Emulsifying hydraulic oil□ (0.02%)	0.5	56	2.27 GPa (0.33 ×□0^6 psi)	32
SAE-10-based mineral oil (0.15%)	0.5	45	Unisteel bearing fatigue test 3.90 GPa (0.57 ×□0^6 psi)	33
SAE-10-based mineral oil (≃0.05%)	0.5	17	Rolling 4-ball 7.52 GPa (1.09 ×□0^6 psi)	34
Emulsifying hydraulic oil (purged with Argon)	1.0 (seawater)	45	Rolling 4-ball 6.89 GPa (1.00 ×□0^6 psi)	35

[a] Water content of oil without added wafer given in parentheses.

where C is the water content in ppm. The exponents of C are in good agreement with the 0.6 in Equation 7. It follows that the Weibull slope increases with increasing water content, suggesting that the lives of those bearings which run the longest before failure are affected most since the water will have a longer time to affect the crack initiation and crack propagation processes.

Most industrial oils contain dissolved water in the range of 50 to 500 ppm and may become further contaminated with moisture from the operating environment. Water molecules, being extremely small compared to the base lubricant and additive molecules, readily diffuse to the tips of microcracks and decompose on the highly reactive newly formed surface to produce atomic hydrogen. The hydrogen diffuses into the metal ahead of the crack, causing hydrogen embrittlement of the steel. The embrittlement not only allows the crack to propagate more readily, but promotes crack branching.[26]

Water-accelerated fatigue and its prevention by lubricant additives has been investigated using a rotating-beam fatigue apparatus.[36] The additives are considered to function by proton neutralization, formation of hydrophobic film, or water sequestration.

Lubricant Type and Lubricant Additives

Lubricant type can significantly affect fatigue life. Fire-resistant fluids lead to an appreciable reduction in life.[37,38] Recent comparative results for several fluids with tapered roller bearings and the Unisteel fatigue test are given in Table 4.

Extreme pressure and antiwear lubricant additives can have a significant influence on

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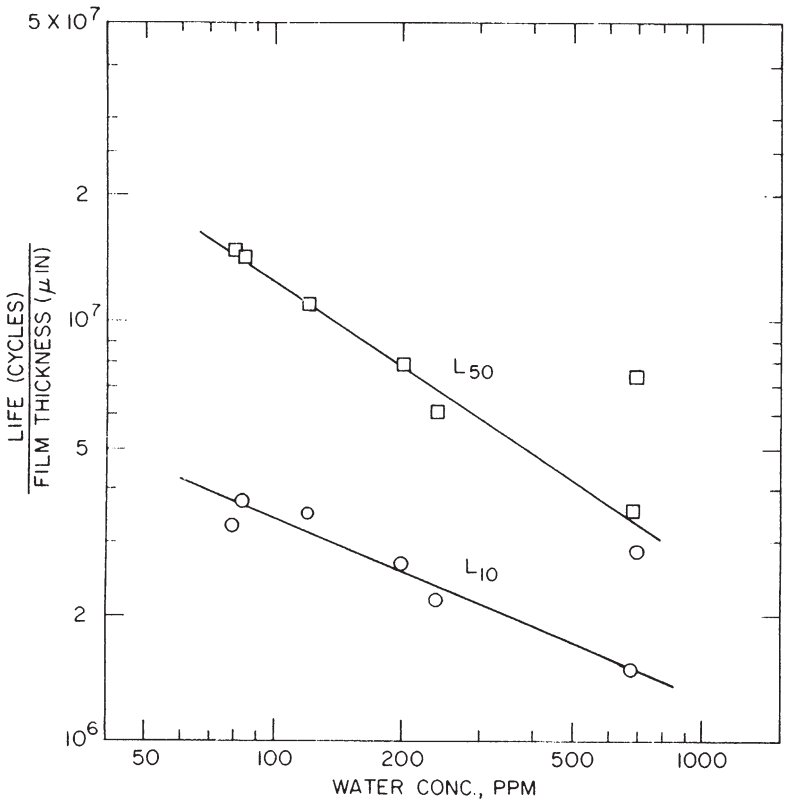

FIGURE 8. Correlation of fatigue life/EHL film thickness ratio with inherent water content for a series of hydraulic fluids.

Table 4
COMPARISON OF RELATIVE FATIGUE LIFE FOR FIRE-RESISTANT FLUIDS

	Tapered roller bearing 1.97 GPa (0.285 × 10^6 psi)[37]	Unisteel 3.88 GPa (0.563 × 10^6 psi)[38]
Mineral oil	1.0	1.0
Phosphate ester	0.49—0.80	0.79
Water-in-oil emulsion	0.31—0.53	0.21
Water glycol	0.14—0.20	0.17
Dilute emulsion, 5/95 oil/water	—	0.06

fatigue life.[26] A sulfur-phosphorus EP additive reduced fatigue life at high values of the specific film thickness, but increased life at low values.[39] Additive response, positive or negative, has been found to be sensitive to oil base stock, additive concentration, and metallurgy.[40] Oxidation of the oil can lead to reduced fatigue life,[41] and the magnitude of reduction is influenced by acid strength.[42] Under combined rolling/sliding conditions, a zinc dialkytphosphorodithioate additive reduced fatigue life to a greater extent at lower stress level than at a higher stress level.[43] Since many bench fatigue tests operate at stress levels that significantly exceed those in field applications, it is important to know the influence of stress level on additive response.

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Table 5
EFFECT OF REAR AXLE LUBRICANTS ON FATIGUE LIFE OF TAPERED ROLLER BEARINGS

SAE Grade	Type of EP additive package	L_{50} life, normalized
90	None	1.00
80	Lead-sulfur	0.24
80	Lead-sulfur	0.34
80	Phosphorus-sulfur	0.32
90	Zinc-phosphorus-sulfur	0.17
90	Zinc-phosphorus-sulfur-chlorine	0.40
90	Phosphorus-sulfur	0.67

Note: 1.03 GPa (150,000 psi) maximum Hertz stress.

From Kepple, R. K. and Johnson, M. F., *Effect of Rear Axle Lubricants on Fatigue Life of Tapered Roller Bearings,* Paper No. 760329, Society of Automotive Engineers, Warrendale, Pa., 1976. With permission.

As a general conclusion, many EP and antiwear additives reduce fatigue life. Table 5 compares the results for a series of rear axle lubricants with different types of EP additives in a tapered roller bearing test.[44] Recently, however, an organophosphonate was reported to provide an increase in fatigue life via the generation of a film on rolling element surfaces.[45]

EROSIVE WEAR

Erosive wear involves loss of material from a solid surface due to the abrasive action, or impingement, of fluids or solid particles suspended in the fluids. If the fluid is corrosive, the phenomenon may be called erosion corrosion. Erosive wear of plain bearings can occur from the rapid flow of a viscous fluid over sharp edges of bearing features.[46] Erosion by solids under lubricated conditions can occur when particles are carried by the oil stream. In the case of plain bearings, erosive wear occurs in the vicinity of the inlet ports.[47]

CAVITATION WEAR

Wear can occur by the high impact pressure resulting from the collapse of vapor and gas bubbles in a liquid. The phenomenon is generally found where the hydrodynamic condition is characterized by a sudden and gross change in pressure resulting in the formation and the collapse of bubbles. Wear of ship propellers constituted one of the first field problems of cavitation damage.

In lubricating films two types of disruption of the continuous liquid phase are recognized: gaseous cavitation and vapor cavitation. Gaseous cavitation results when the pressure to which the lubricant is subjected falls below the saturation pressure of dissolved gases. Vapor cavitation results when the pressure in a liquid falls below the vapor pressure of the liquid causing local boiling and the formation of bubbles which then collapse as the pressure is increased. Gaseous cavities form and collapse more slowly than vapor cavities, thereby generally causing less surface damage.[46,48]

Film rupture and the fundamental aspects of the formation of cavities or bubbles in plain bearings are found in a number of papers in the Proceedings of the First Leeds-Lyon Symposium on Tribology.[49] Cavitation can influence the performance of dynamically loaded.

Film rupture and the fundamental aspects of the formation of cavities or bubbles in plain bearings are found in a number of papers in the Proceedings of the First Leeds-Lyon Symposium on Tribology.[49] Cavitation can influence the performance of dynamically loaded journal bearings[50] and externally pressurized journal bearings.[51] The effect is one of lower load capacity, lower film thickness, and the onset of surface damage. The side plates in gear pumps may undergo surface damage and wear due to cavitation.

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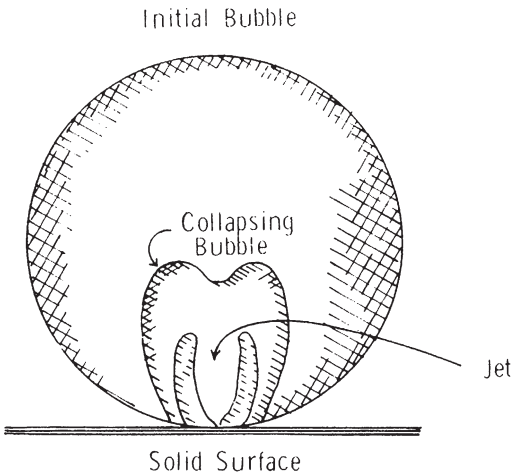

FIGURE 9. Collapse of a bubble. (From Plesset, M. S. and Chapman, R. B., *Collapse of an Initially Spherical Vapor Cavity in the Neighborhood of a Solid Boundary,* California Institute of Technology, Pasadena, 1970. With permission.)

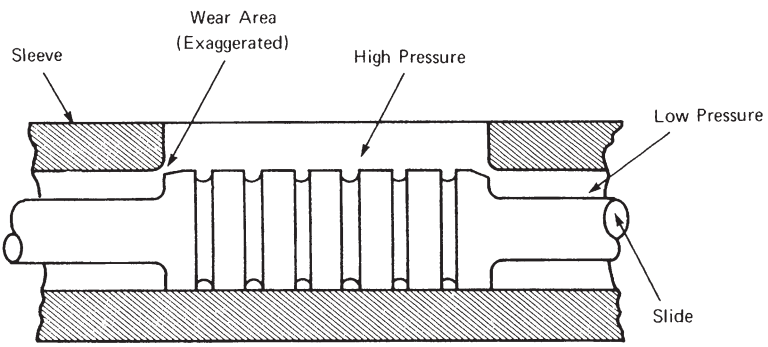

FIGURE 10. Electrochemical wear in aircraft servo valves. (From Beck, T. R., Mahaffey. D. W., and Olsen, J. H., *J. Basic Eng.,* 92, 782, 1970. With permission.)

Cavitation may be important in wear of rolling contact bearings.[52] Resistance to fatigue in a four-ball rolling contact test correlated with the resistance to pitting in a cavitation erosion test. A similar conclusion has been reached that cavitation erosion is a fatigue process due to the related impacts of liquid jets as a result of bubble collapse.[53]

The detailed mechanism of cavitation erosion is still unknown. Figure 9 shows the collapse of a bubble with the formation of a high-velocity microjet in the center.[54] The similarity of these jets to liquid impingement suggests that cavitation wear and fluid erosion are similar. Surface tension increases the rate of collapse, while compressibility, viscosity, and the presence of noncondensable gases tend to decrease the rate.[55]

ELECTROCHEMICAL WEAR

A less frequent type of wear is that caused by electrochemical reactions. Wear of aircraft hydraulic servo valves in the presence of a phosphate ester fluid has been ascribed to the generation of an electrokinetie or streaming current.[56] As shown in Figure 10 the wear occurs

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on the upstream side of the valve, and it occurs most rapidly when the valve is in the null position with a large pressure drop (3000 psi) across the small orifice. Theory hypothesizes that fluid flow will sweep free charges in the diffuse outer regions of the electrical double layer, thereby setting up an electrokinetic potential between the solid and the fluid outside the diffuse layer. The conservation of charge imposes a current flow between the metal and fluid, known as the wall current, which causes electrochemical reactions.

For this type of wear to occur, the fluid must meet two conditions: the electrical double layer is thin compared to the hydrodynamic boundary layer, and the conductivity of the fluid is relatively low compared to that of the metal. Low-conductivity fluids violate the first condition, while high-conductivity fluids fail the second. The phosphate ester evidently met both conditions.

Wear can be investigated in water-based emulsion lubricants by electrochemical methods.[57] As an example, the potential in a cationic emulsion was used to distinguish between adhesive and corrosive wear of a chromium-plated yarn guide.[58]

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